Reply to Comments from Referee #1

1. In the section of non-ferrous smelting, I suggest some more discussion about mercury use and emission from golden smelting should be added.

Response:

We have added the discussion on mercury speciation in the gold smelting process based on our recent measurements. Please see the updated Table 2, Lines 272-278 on Page 10 and Lines 389-392 on Page 14 in the revised manuscript:

"The case in the industrial gold smelting process is an exception. Based on the recent on-site measurements, only 85% of the mercury in gold concentrate evaporates into the flue gas with the roasting temperature at 600°C (Yang, 2015). The low mercury release rate in the tested gold smelter is due to the chemical properties of mercury and gold. According to a previous study (Li, 1990), mercury at certain chemical speciation in gold ores only releases when the temperature exceeds 780°C."

"The mercury speciation profile (Hg^0:Hg^{2+}:Hg_p) in the exhausted flue gases in gold smelters with the double-conversion-double-absorption process is estimated to be 32:57:11 (Yang, 2015)."

Dr. Mei Yang has contributed to this part, so we have added her as a co-author.

References:

Li, J.: Distribution features of mercury compounds in gold deposits, Geology and Exploration, 11, 46–51, 1990.

Yang, M.: Research on atmospheric mercury emission inventory and control technology of gold production in China, Postdoctoral work report, Tsinghua University, Beijing, China, 2015.

2. Except for sources associated with combustion or high temperature industrial process, additional discussion and summary for some other Hg emission source are suggested to be added to make the critical review more complete and integrated.

Response:

We have added discussion on waste incineration, biomass burning, cremation and

PVC production to Section 5 (previous Section 6 because iron and steel production has been combined to this section). Please see the updated Section 5 in the revised manuscript:

"In this section, the behavior of mercury in flue gases from other emission sources, including iron and steel production, waste incineration, biomass burning, cremation, and PVC production, are introduced. Although there are still other mercury emission sources not discussed in this study, such as oil combustion, few field measurements are available for mercury speciation and transformation inside these sources."

"5.2 Mercury speciation and transformation in flue gas from waste incineration

Waste incineration is a potential predominant source in the global mercury emission inventory. The major incineration types are municipal solid waste (MSW) incineration, medical waste incineration and industrial/hazardous waste incineration. A significant proportion of mercury (80–96%) in the MSW releases from the incinerator into the flue gas is in the form of Hg^0 at 850–1000°C (Park et al., 2008). Grate furnace combustor (GFC) and circulation fluidized bed combustor (CFBC) are the two most commonly used incinerators. The flue gas from CFBC has a larger proportion of Hg_p than that from GFC. Typical APCDs for incinerators are combinations of semi-dry or dry flue gas deacidification (SD-FGD or D-FGD) for SO_2 and HCl removal and dust controller (e.g., WS+ESP, FF, FF+WS, etc.). SCR is sometimes used as well for NO_x control. Activated carbon injection (ACI) is used for the control of persistent organic pollutants (POPs), which is required for incinerators in China.

The overall mercury removal efficiency of the APCDs for MSW incineration ranges from 60% to over 99% (Zhang et al., 2008; Takahashi et al., 2012). Previous studies in Europe and the USA indicated that the Hg^{2+} proportion in the exhausted flue gas ranges from 75% to 85%(Pacyna and Münch, 1991; Carpi, 1997). A Korean study found the Hg^{2+} proportion in MSW incinerators to be in the range of 78–89%, and that in industrial waste incinerators are even as high as 96.3–98.7% (Park et al., 2008). Kim et al. (2010a) tested two medical waste incinerators with SD-FGD+FF+WS and got the Hg^0 proportion to be 43.9% and 96.8% respectively. A Japanese study showed that an industrial waste incinerator with WS and wet ESP has the Hg^0 proportion of 92.7% (Takahashi et al., 2012). Based on field measurements in eight MSW incinerators in China, Chen et al. (2013) found that average Hg^{2+} proportion in flue gas from the outlet of GFC+SD-FGD+ACI+FF is 96%, while that for CFBC+SD-FGD+ACI+FF is 64%. High chlorine content in the waste results in high Hg^{2+} proportion in the flue gas. Limestone slurry or powder sprayed in SD-FGD or D-FGD absorbs a large amount of Hg^{2+} and activated carbon adsorbs a large amount of both Hg^0 and Hg^{2+}. Particles from SD-FGD and ACI are captured by the downstream FF. Hg_p is removed by all types of dust controllers. The high Hg^{2+} formation rate due to the oxidative condition in flue gas and the high Hg^{2+} removal rate by APCDs (especially SD-FGD, FF and ACI) cause the significant variation in mercury speciation profiles for incinerators."

"5.3 Mercury speciation and transformation in flue gas from biomass burning

Biomass burning mainly includes biomass fuel burning and open biomass burning. Biomass fuel can be divided into fuel woods, crop residues and biomass pellets. Usually, there is no APCD for biomass burning. Huang et al. (2011) tested four different types of wood fuels and found the Hg^0 proportion to be 95–99% and the rest is basically Hg^{2+}. Wei (2012) found that Hg^0 in flue gas from biomass burning is 70–90% of total mercury while that of Hg^{2+} ranges from 5% to 9%. Hg_p proportion differs a lot between different biomass fuel types: 12%, 25% and 1% for fuel wood, crop residues and biomass pellets, respectively. Hu et al. (2012) differentiated the emission factors for biomass burning and cooking/space heating in rural areas to be 0.035 and 0.515 g Hg/t biomass burned, respectively. W. Zhang et al. (2013) tested 25 types of fuel wood, 8 types of crop residues and 2 types of biomass pellets, and found that the mercury emission rate during biomass burning is 78–99% while the remainder stays in the residue. The mercury speciation profile (ratio of Hg^0, Hg^{2+} and Hg_p to total Hg) for fuel wood was 76%, 6% and 18%, and that for crop residue was similar (73%, 4% and 23%). However, the speciation profile for biomass pellets is quite different. Due to the more complete combustion, Hg^0 accounts for as high as 97% in the flue gas from of biomass pellets combustion. W. Zhang et al. (2013) calculated mercury emission from biomass burning in China and gave the shares of Hg^0, Hg^{2+} and Hg_p at 74%, 5% and 21%, respectively. Open biomass burning generally involves forest wildfires, grassland/savanna wildfires, and agriculture residue burning. Friedli et al. (2003) investigated the mercury speciation from burning of temperate North American forests through both laboratory and airborne measurements. Their research showed that the dominant species is Hg^0, accounting for 87–99% of the total mercury, and the rest is mainly Hg_p."

"5.4 Mercury speciation and transformation in flue gas from cremation

Researches on mercury speciation and transformation in flue gas from cremation are very limited. Takaoka et al. (2010) conducted field measurements in seven crematories in Japan, two of them without any APCDs, one with ESP and four with FF for particle control. Advanced APCDs such as catalytic reactor and activated carbon filter are installed in three of the tested crematories. In the exhausted flue gases, Hg^0 is averagely the dominant mercury species but with significant variation (25–99%). Extremely large uncertainties exist in this sector due to the large diversity of mercury content in human body and whether the dental amalgam is applied."

"5.5 Mercury speciation and transformation in flue gas from PVC production

Aside from combustion and some high-temperature industrial processes, there are some other processes with intentional mercury use that also have mercury emissions. The production of polyvinyl chloride (PVC) with the calcium carbide process utilizes a catalyst containing large amounts of mercury. Ren et al. (2014) conducted on-site measurements in a PVC production line and found that 71.5% of the total mercury was lost from the catalyst, most of which was recovered by the mercury remover, accounting for 46% of the total mercury. The total mercury emitted to the atmosphere only accounted for less than 1% of the total mercury in the catalyst. The speciation tests indicated that most of the mercury escaped from the catalyst was Hg^0, as no Hg^{2+} was detected virtually."

Added references:

Friedli, H. R., Radke, L. F., Lu, J. Y., Banic, C. M., Leaitch, W. R., and MacPherson, J. I.: Mercury emissions from burning of biomass from temperate North American forests:laboratory and airborne measurements, Atmos. Environ., 37, 253–267, 2003.

Huang, J. Y., Hopke, P. K., Choi, H.-D., Laing, J. R., Cui, H. L., Zananski, T. J., Chandrasekaran, S. R., Rattigan, O. V., and Holsen, T. M.: Mercury (Hg) emissions from domestic biomass combustion for space heating, Chemosphere, 84, 1694–1699, 2011.

Ren, W., Duan, L., Zhu, Z. W., Du, W., An, Z. Y., Xu, L. J., Zhang, C., Zhuo, Y. Q., and Chen, C. H.: Mercury transformation and distribution across a polyvinyl chloride (PVC) production line in China, Environ. Sci. Technol., 48(4), 2321–2327, 2014.

Takaoka, M., Oshita, K., Takeda, N., and Morisawa, S.: Mercury emission from crematories in Japan, Atmos. Chem. Phys., 10, 3665–3671, 2010.

Reply to Comments from Referee #2

1. Section 2.2.4 seems a bit out of place. You are going through the figure and the APCD's, and this section focuses on industrial boilers, where the sections before and the section after is for CF power plants. Consider making this one last of Section 2.2.X.

Response:

This sub-section has been moved to the last of this section as suggested.

2. Section 2.2.5 isn't in the figure. Perhaps it is not appropriately put there? I was just expecting it to be there.

Response:

Section 2.2.5 is indeed in the figure. We used "FGD" which is not consistent with the text. We have changed it to "WFGD". Please see the modified Fig. 1.

3. Page 32899, line 13; bonds instead of bounds.

Response:

Modification has been made.

4. Page 32900, DCA isn't defined or in the figure.

Response:

The DCA towers mean dehydration tower, conversion tower and absorption tower, all of which are units in the acid plant. Therefore, we have changed it to "acid plant" in the revised manuscript.

5. Page 32901, Line 8. "FGS uses…". Again, I am no engineer, but I thought these used calcium carbonate and the like to scrub sulfur out of these streams in wet scrubbers.

Response:

Unlike WS or WFGD for SO_2 control in coal combustion, FGS in non-ferrous metal smelters uses diluted sulfuric acid to capture SO_2 and SO_3. The yield from FGS is waste acid, which will be treated to acid sludge. This point has been added to this part. Please see Lines 322-325 on Page 12 in the revised manuscript.

6. Page 32903, line 3, reference Wu et al., 2006 isn't in the references.

Response:

This reference has been added to the reference list.

7. Page 32910, line 11-12, sentence ", and found that the mercury" is unclear to me what the release rate means. Do you mean that the emission is 70-90% and the remainder is in the ash? Just unclear.

Response:

We have changed the expression of this sentence. Please see Lines 587-588 on Page 21 in the revised manuscript:

"… and found that the mercury emission rate during biomass burning is 78–99% while the remainder stays in the residue"

8. Section 4 is very difficult to follow. You should definitely point people to the figure (#4) at the beginning of the discussion for better understanding by the reader. I agree to understand the system, much discussion is needed. However, an alternative is to shorten the discussion, making the broad points that: 1. Hg in the raw materials comes out in the roasting process, 2. by using the flue gas to preheat the raw materials and coal, the Hg is recycled and is enriched along the way, and 3. that the operational modes vary dramatically and the emissions and ratios will be highly different and have to be accounted for in emission databases. I agree it is complicated and so variable that the process takes a bit of discussion to explain it.

Response:

We thank the reviewer for the valuable suggestion. We have revised Sections 4.1, 4.2 and 4.3 in our manuscript according to this comment. The introduction of cement production process and the mercury behavior have been simplified. The three points advised by the reviewer have been emphasized and highlighted in the manuscript. Figure 4 has also been introduced in the beginning of our discussion. Please see the updated Section 4 in the revised manuscript:

"Precalciner process is usually composed of the raw mill system, the coal mill system, the kiln system and the kiln head system. Raw materials are ground and homogenized in the raw mill system. The fuel, usually coal, is prepared in the coal mill system including coal mill and FF. The kiln system for the production of cement clinker includes the preheater, the precalciner and the rotary kiln. The prepared raw materials, namely raw meal, enter the kiln system from one end of rotary kiln (kiln tail), and the coal powder is brought into the kiln system by air from the other kiln end (kiln head). The solid materials flow in opposite direction with the flue gas. The flue gas from kiln tail is used to preheat raw materials in raw mill and coal in coal mill. The flue gas from kiln head is de-dusted and then emitted into the atmosphere. All the dust collected by dust collector is recycled to kiln system."

"The mercury behavior in cement production process is summarized as three stages: vaporization, adsorption and recycling (Sikkema et al., 2011) (see Fig. 4). At the vaporization stage, mercury in raw materials and fuel is vaporized into flue gas in the kiln system. Then part of the mercury in flue gas is captured by raw materials in the raw mill and coal in the coal mill when the flue gas is used to preheat solid materials, and part of the mercury in flue gas is also collected in the dust collector with dust. This process is called the adsorption stage. Finally, the mercury is cycled back into the kiln system with raw materials, coal and collected dust, which is the recycling stage."

The first two sentences of Section 4.3 have been deleted.

9. Further, in figure 4, I would suggest: a. Add a "clinker out" yellow arrow b. Add a box on the green arrow of mercury from the coal mill and collector that shows it is preheated as described in the text.

Response:

Figure 4 has been revised as suggested by the reviewer.

10. I would restate in Section 4 at the end, that these process are so highly variable that the emissions inventories are likely to be wrong, or something to that effect.

Response:

We have added some discussion about the point commented by the reviewer. Please see Lines 501-506 on Page 18 in the revised manuscript:

"As discussed above, the mercury speciation and emission are largely variable because of the complicated mercury cycling and operational modes of the cement clinker production process. Previous estimates of mercury emission and speciation from cement clinker production have large uncertainties. More studies including field tests should be conducted to further understand the mechanism of mercury speciation and transformation in cement production."

11. Section 5; many readers will not know what sintering is. I would use a short parenthetical to define.

Response:

We have explained the sintering process clearer as suggested by the reviewer:

"…roasted in the sintering machine, namely the sintering process."

12. References: a. I did not find Eriksen used. b. Lopez-Anton is referenced as 2007 in the text; check this one c. Takahashi is referenced as 2010 in the paper; check this one.

Response:

The reference of Eriksen et al. has been removed. Both López-Antón et al. (2007) and López-Antón et al. (2011) have been used in the paper. López-Antón et al. (2007) has been added to the reference list. The year of Takahashi et al. should be 2012, which has been modified in the text.

13. Table 1: I would add to the title Table 1. "Average (Range)" Speciation profile of mercury emissions from coal combustion "By Boiler Type and Control Technology (%)".

Response:

Modification has been made accordingly.

14. Table 2: same comment.

Response:

Modification has been made accordingly.

15. Table 3: same comment.

Response:

Modification has been made accordingly.

16. Table 4: I would add lines between the countries or regions so that they are more easy to compare. Hard with no dividing lines.

Response:

The original table has lines in between. It is probably the requirement of the editorial office.

17. Figure 1. a. APH isn't defined, and not sure what it is b. The influence of mercury by the FGD was not discussed in the paper. Perhaps there is none, but you have the chemical transformations in the table, and would imply that there are implications to the mercury reduction (or addition), and the fractionation between the three Hg types.

Response:

APH means air preheater. We have replaced it with full name. The "FGD" should be "WFGD" as explained in Comment 2. We have changed it in the figure.

18. Figure 2. Minor points here a. The arrows between the boxes; is there any meaning to the different sized arrows. If yes, describe in a caption. If no, make them all the same size. b. Same comment with blue arrows and size. c. Just a question: why

is the liquid phase in the Flue Gas Purification box not represented the same way? Is it water droplets? Should it be represented the same way? d. Same box. Does Hg0 really get removed by the spray? Is this why the arrow size is so small? too little affinity for water? e. Bottom box: in other boxes the Hg0 arrow goes both ways. Is it different here? Only one way?

Response:

We have revised all the arrows to the same size and deleted the sprayers to make it consistent.

Previous studies have observed liquid Hg^0 in the removed waste acid (Wang, 2011). Researchers deduce that the decreased temperature in the flue gas purification system is one important reason for gaseous Hg^0 condensation and removal by water spray. However, according to the saturated vapor pressure of Hg^0, this phenomenon happens when the gaseous mercury concentration is very high, approximately 29–62 mg/m^3 in the flue gas purification system. Currently, gaseous mercury concentration in this system in most of the Chinese nonferrous smelters can't reach this value. Therefore, we believe the Hg^0 removal by spray is not a predominant mechanism in the flue gas purification system, but we keep this mechanism in the figure. This point has also been added to the text.

Studies on the mercury behavior in the FGD system of nonferrous metal smelters are limited. According to studies in coal-fired power plants, Hg^{2+} in the FGD gypsum might be reduced to Hg^0 in the FGD system. We have added this mechanism into this figure.

Reference:

Wang, Q. W.: New technology for treatment of mercury-containing acidic wastewater from gas washing process in lead and zinc smelting by biologics, Ph.D. thesis, Central South University, Changsha, China, 2011.

19. Figure 4: I would add "and flow" to the caption after transformation.

Response:

Modification has been made accordingly.

Reply to Comments from Referee #3

1. “Environmental diplomatic affairs”?

Response:

We have revised it to “global environmental issues”.

2. “Annex D for Article 8 of the Minamata Convention”. Please provide Reference to this.

Response:

We have added the reference:

“United Nations Environment Programme (UNEP): Minamata Convention on Mercury, available at: http://www.mercuryconvention.org/Convention/tabid/3426/Default.aspx (last access: 1 February 2016), 2013b.”

3. “Operationally defined chemical forms” Is this the right terminology?

Response:

We have modified it to “major chemical forms”.

4. Authors present “The dust cake layer also facilitates oxidation of Hg0” How does dust cake layer facilitate oxidation? It should capture Hg instead! Needs clarification. Please provide reference of your argument.

Response:

The fly ash on the dust cake directly captures Hg^{2+} and facilitates the oxidation of Hg^0. We have added reference to this argument.

Reference:

Wang, F. Y., Wang, S. X., Meng, Y., Zhang, L., Wu, Q. R., and Hao, J. M.: Mechanisms and roles of fly ash compositions on the adsorption and oxidation of *mercury in flue gas from coal combustion, Fuel, 163, 232–239, 2016.*

5. 2.3 Reference to Table 1 is missing. And in the discussion part of the Table there are too many generalizations without supporting data. What are these data for, which coal types? Anthracite? Bituminous? Lignite?? What was the chlorine content? Those will have significant implications in Hg speciation. Actually, there are bulky data available in literature from field tests and Review paper should include those.

Response:

We have added all the references to Section 2.3. Section 2.3 is a summary of the ultimate speciation profiles for Section 2. The influence of coal quality (e.g. chlorine content, mercury content, etc.) on mercury speciation from coal combustion is discussed in Sections 2.1 and 2.2. The coal type does not directly influence mercury speciation. It is the coal quality of different coal types that takes the effect. We have included about 20 papers with field tests.

6. 2.2.5 Mercury transformation during wet flue gas desulfurization (WFGD): In this section, authors have mixed up information of all the plants together, without taking care of the upstream APCDs configuration. As authors have presented in the earlier section that APCDs configuration has important effect on speciation, authors have missed to explain the effect of upstream APCDs e.g. ESP and SCR in Hg removal in FGD. Needs careful review of these.

Response:

We have added the influence of SCR to this part. Please refer to Lines 216-218 on Page 8 in the revised manuscript:

"The applications of high-chlorine coal, SCR and halogen addition can increase the Hg^{2+} proportion in flue gas before WFGD, which will enhance the overall mercury capture efficiency of WFGD."

The influence of ESP is not clear. Because the proportion of either Hg^{2+} or Hg^0 can increase after ESP due to the co-existence of Hg^0 oxidation and Hg^{2+} reduction inside ESP, which has been discussed in Section 2.2.2.

7. Hg emission from MSW incinerators are one of the major sources, however, only little has been covered about it. No coverage on medical, hospital waste incineration? No discussion on hazardous waste incineration? This makes the review incomplete!

Response:

We have carefully modified this part and added results on mercury speciation in medical and industrial/hazardous waste incinerators. Please see Section 5.2:

"Waste incineration is a potential predominant source in the global mercury emission inventory. The major incineration types are municipal solid waste (MSW) incineration, medical waste incineration and industrial/hazardous waste incineration. A significant proportion of mercury (80–96%) in the MSW releases from the incinerator into the flue gas is in the form of Hg^0 at 850–1000°C (Park et al., 2008). Grate furnace combustor (GFC) and circulation fluidized bed combustor (CFBC) are the two most commonly used incinerators. The flue gas from CFBC has a larger proportion of Hg_p than that from GFC. Typical APCDs for incinerators are combinations of semi-dry or dry flue gas deacidification (SD-FGD or D-FGD) for SO_2 and HCl removal and dust controller (e.g., WS+ESP, FF, FF+WS, etc.). SCR is sometimes used as well for NO_x control. Activated carbon injection (ACI) is used for the control of persistent organic pollutants (POPs), which is required for incinerators in China. The overall mercury removal efficiency of the APCDs for MSW incineration ranges from 60% to over 99% (Zhang et al., 2008; Takahashi et al., 2012). Previous studies in Europe and the USA indicated that the Hg^{2+} proportion in the exhausted flue gas ranges from 75% to 85% (Pacyna and Münch, 1991; Carpi, 1997). A Korean study found the Hg^{2+} proportion in MSW incinerators to be in the range of 78-89%, and that in industrial waste incinerators are even as high as 96.3－98.7% (Park et al., 2008). Kim et al. (2010a) tested two medical waste incinerators with SD-FGD+FF+WS and got the Hg^0 proportion to be 43.9% and 96.8% respectively. A Japanese study showed that an industrial waste incinerator with WS and wet ESP has the Hg^0 proportion of 92.7% (Takahashi et al., 2012). Based on field measurements in eight MSW incinerators in China, Chen et al. (2013) found that average Hg^{2+} proportion in flue gas from the outlet of GFC+SD-FGD+ACI+FF is 96%, while that for CFBC+SD-FGD+ACI+FF is 64%. High chlorine content in the waste results in high Hg^{2+} proportion in the flue gas. Limestone slurry or powder sprayed in SD-FGD or D-FGD absorbs a large amount of Hg^{2+} and activated carbon adsorbs a large amount of both Hg^0 and Hg^{2+}. Particles from SD-FGD and ACI are captured by the downstream FF. Hg_p is removed by all types of dust controllers. The high Hg^{2+} formation rate due to the oxidative condition in flue gas and the high Hg^{2+} removal rate by APCDs (especially SD-FGD, FF and ACI) cause the significant variation in mercury speciation profiles for incinerators."

8. Conclusion: "Hg0 is the predominant mercury species in exiting flue gases from coal-fired power plants due to the high Hgp removal efficiency of ESP or FF and the high Hg2+ removal efficiency of WS or WFGD." The predominant Hg0 is not only because Hgp removal in ESP or FF and the high Hg2+ removal in FGD, this is also because the emission of Hg0 is dominant in boiler outlet.

Response:

We have added one sentence to clarify this point and modified the expression of this sentence. Please see Lines 650-655 in the revised manuscript:

"The initial speciation of mercury after the boiler, smelter or kiln varies significantly because of the diverse qualities of coals or raw materials. Nearly all mercury in coal is released into the flue gas in the form of Hg^0 during combustion. Hg^0 is the predominant mercury species in exiting flue gases from coal-fired power plants mainly due to the high Hg_p removal efficiency of ESP or FF and the high Hg^{2+} removal efficiency of WS or WFGD."

Mercury transformation and speciation in flue gases from anthropogenic emission sources: A critical review

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Abstract. Mercury transformation mechanisms and speciation profiles are reviewed for mercury formed in and released from flue gases of coal-fired boilers, non-ferrous metal smelters, cement plants, iron and steel plants, municipal solid waste incinerators, and biomass burning. Mercury in coal, ores and other raw materials is released to flue gases in the form of Hg^0 during combustion or smelting in boilers, kilns or furnaces. Decreasing temperature from over 800°C to below 300°C in flue gases leaving boilers, kilns or furnaces promotes homogeneous and heterogeneous oxidation of gaseous elemental mercury (Hg^0) to gaseous divalent mercury (Hg^{2+}), with a portion of Hg^{2+} adsorbed onto fly ash to form particulate-bound mercury (Hg_P). Halogen is the primary oxidizer for Hg^0 in flue gases, and active components (e.g., TiO_2, Fe_2O_3, etc.) on fly ash promote heterogeneous oxidation and adsorption processes. In addition to mercury removal, mercury transformation also occurs when passing through air pollution control devices (APCDs), affecting the mercury speciation in flue gases. In coal-fired power plants, selective catalytic reduction (SCR) system promotes mercury oxidation by 34–

85%, electrostatic precipitator (ESP) and fabric filter (FF) remove over 99% of Hg_p, and wet flue gas desulfurization system (WFGD) captures 60–95% of Hg^{2+}. In non-ferrous metal smelters, most Hg^0 is converted to Hg^{2+} and removed in acid plants (APs). For cement clinker production, mercury cycling and operational conditions promote heterogeneous mercury oxidation and adsorption. The mercury speciation profiles in flue gases emitted to the atmosphere are determined by transformation mechanisms and mercury removal efficiencies by various APCDs. For all the sectors reviewed in this study, Hg_p accounts for less than 5% in flue gases. In China, mercury emission has a higher Hg^0 fraction (66–82% of total mercury) in flue gases from coal combustion, in contrast to a greater Hg^{2+} fraction (29–90%) from non-ferrous metal smelting, cement and iron/steel production. The higher Hg^{2+} fractions shown here than previous estimates may imply stronger local environmental impacts than previously thought, caused by mercury emissions in East Asia. Future research should focus on determining mercury speciation in flue gases from iron and steel plants, waste incineration and biomass burning, and on elucidating the mechanisms of mercury oxidation and adsorption in flue gases.

1 Introduction

Atmospheric mercury is one of the key focuses in the global environmental issues in recent years owing to its toxicity, persistence and long-range transportability. The international treaty on mercury, the Minamata Convention, was adopted worldwide in October 2013 aiming to reduce mercury release into the immediate environments. Coal combustion, cement clinker production, and primary production of ferrous and non-ferrous metals, are predominant sources of global anthropogenic mercury emission (UNEP, 2013a). Aside from coal-fired power plants, coal-fired industrial boilers, cement clinker production facilities, and smelting and roasting processes used in the production of non-ferrous metals (lead, zinc, copper and industrial gold), waste incineration facilities, in terms of their rapid growth, are also on the list of key point sources in Annex D for Article 8 of the Minamata Convention (UNEP, 2013b).

Mercury has three major chemical forms: gaseous elemental mercury (Hg^0), gaseous oxidized (or reactive) mercury (Hg^{2+}) and particulate-bound mercury (Hg_p). Hg^0, the most stable form, accounts for over 90% of the total mercury in the atmosphere. Its residence time is estimated to be several months to over one year (Schroeder and Munthe, 1998; Lindberg et al., 2007; Fu et al., 2012), but could be as short as hours to weeks under specific environmental conditions (Gustin et al., 2008). Hg^{2+} has high water-solubility and thus can be easily scavenged into droplets and adsorbed to surfaces followed by wet and dry deposition. The short residence time (hours to days) of Hg^{2+}leads to more prominent local environmental impacts. Hg_p has a residence time of hours to weeks, and mercury on finer particles can be transported for long distances (Schroeder and Munthe, 1998). Hg^{2+} and Hg_p are also referred to as reactive mercury (RM) due to their high surface reactivity (Rutter and Schauer, 2007). Mercury speciation profiles in the exhausted flue gases from key sources determine the behavior of atmospheric mercury in the ambient air, while the profiles in the pipeline flue gases are crucial to mercury emission controls.

Different emission sources have different mercury speciation profiles. Even for the same emission category, the profile varies significantly when different combinations of air pollution control devices (APCDs) are applied or different types of fuels or raw materials are used. Different countries or regions have distinguished mercury speciation profiles for similar emission sources because of APCD preferences and fuel (or raw material) properties. The profiles can vary with time as advanced air pollution control technologies are implemented. Inventory experts tend to use more localized and up-to-date profiles from on-site measurements of mercury emission sources. Walcek et al. (2003) employed three sets of profiles respectively for fuel combustion, waste incineration and other manufacturing processes, and found the overall relative emission proportions (REPs) among Hg^0:Hg^{2+}:Hg_p species for the 1996 inventory of eastern North America to be 47:35:18. Streets et al. (2005) accomplished a more detailed profile list for different source categories with profiles under different APCDs for coal combustion, and obtained the overall REPs for China in 1999 which were 56:32:12. Pacyna et al. (2006) developed the 2000 mercury emission inventory for Europe and evaluated the overall REPs to be 61:32:7. The REPs for anthropogenic mercury emissions from Korea in 2007 were estimated to be 64:29:7 (Kim et al., 2010a), and those for the 2006 inventory of Australia were 77:17:6 (Nelson et al., 2012). Our recent study updated the anthropogenic mercury emission inventory of China to the calendar year 2010 based on an abundant database of field measurements, and the REPs of the overall mercury speciation profile were 58:39:3 (Zhang et al., 2015). Although the ratio of Hg^0 to Hg^{2+} seems to be close to the results from Streets et al. (2005), the sectoral profiles have changed significantly because of the implementation of APCDs in key sources in China. Results from on-site measurements in Chinese power plants, non-ferrous metal smelters and cement plants have substantially improved the speciation profiles.

Mercury speciation profiles of major emission sources in the world have remarkable influences on the assessment of long-range transport of atmospheric mercury. This paper provides a critical review of mercury speciation in flue gases from major anthropogenic emission sources, and elaborates the process of initial mercury release in boilers, kilns or furnaces to its transformation in the flue gases across APCDs. Key factors during the emission process for each source are identified for the enhancement of existing control technologies. Profiles of mercury speciation in different countries and regions are compared by sectors to assess their local and regional environmental impacts.

2 Mercury speciation and transformation in flue gases from coal combustion

2.1 Mercury speciation in flue gas from coal combustion

Nearly all mercury in coal is released into the flue gas in the form of Hg^0 during combustion over 1000°C. With the decrease of flue gas temperature out of the boiler, a portion of Hg^0 is oxidized to Hg^{2+} mainly by active atomic Cl generated from HCl, Cl_2 or HOCl (Senior et al., 2000). Niksa et al. (2001) discovered that the cycling of atomic Cl is the dominant mechanism of Hg^0 oxidation. This process, including homogeneous and heterogeneous reactions, is driven by thermodynamic equilibrium, but restricted by reaction kinetics (Widmer et al., 2000). Based on the results from bench-scale experiments, L. Zhang et al. (2013a) found that lower total mercury concentration and higher chlorine concentration in flue gas lead to higher Hg^0 oxidation rate. The results from Sterling et al. (2004) showed that SO_2 and NO in flue gas inhibit the oxidation of Hg^0. The homogeneous reaction mechanism usually underestimates the oxidation rate because heterogeneous reactions on fly ash play a more important role under low temperatures (100°C to 300°C). Heterogeneous processes not only accelerate the oxidation of Hg^0 but also contribute to the adsorption of Hg^{2+} onto fly ash to form Hg_p. Bhardwaj et al. (2009) found that specific surface area (SSA), loss on ignition (LOI) and average particle size positively correlated with both the Hg^0 oxidation and the Hg^{2+} adsorption. Inorganic components such as CuO, TiO_2 and Fe_2O_3 also have significant impacts on the mercury oxidation and adsorption processes (Dunham et al., 2003; Norton et al., 2003; López-Antón et al., 2007).

According to 30 previous on-site measurements in coal-fired power plants and industrial boilers (Kellie et al., 2004; Duan et al., 2005; Lee et al., 2006; Zhou et al., 2006; Chen et al., 2007; Yang et al., 2007; Chen et al., 2008; Wang et al., 2008; Zhou et al., 2008; Kim et al., 2010b; Wang et al., 2010a; Zhang et al., 2012a; L. Zhang et al., 2013a), mercury speciation after the boiler and before APCDs is mainly determined by coal properties, specifically chlorine, mercury and ash contents in coal. Chlorine and mercury contents have the most significant impacts on the percentage of Hg^{2+} in total mercury, while mercury and ash contents highly influence the proportion of Hg_p in total mercury in flue gas. The proportions of Hg^0, Hg^{2+} and Hg_p in the flue gas released from a pulverized-coal (PC) boiler, averaged 56%, 34% and 10%, respectively. However, Hg^{2+} proportion ranged from 5% to 82% while Hg_p proportion ranged from 1% to 28%. Besides the coal properties, the boiler type also affects mercury speciation in flue gas. A circulating fluidized bed (CFB) boiler can generate as high as 65% of Hg_p in flue gas due to more sufficient contact between gaseous phase mercury and fly ash inside the boiler (Zhang, 2012).

2.2 Mercury transformation across APCDs for coal combustion

2.2.1 Mercury transformation during selective catalytic reduction (SCR)

Figure 1 shows mercury transformation and removal processes across APCDs in coal-fired power plants. The first APCD after the boiler could be the SCR system if applied for NO_x control. The operation temperature in a SCR is typically 300–400°C. SCR catalysts, usually composed of V_2O_5, WO_3 and TiO_2, significantly promote the Hg^0 oxidation process and increase Hg^{2+} level for downstream removal in PM and SO_2 control devices (Niksa and Fujiwara, 2005). Laboratory-scale studies (Lee et al., 2003; Bock et al., 2003) showed that Hg^0 oxidant inside SCR is the atomic Cl. The Hg-Cl redox chemistry and the NO-NH_3 redox chemistry occur simultaneously on the active sites of SCR catalyst (L. Zhang et al., 2013b). Therefore, the reaction system in SCR is complicated and influenced by a number of factors. Machalek et al. (2003) pulled subbituminous-derived flue gas into a pilot-scale SCR system and found that the Hg^0 oxidation extent decreased from 40% to 5% when the space velocity (SV) of SCR was increased from 3000 to 7800 hr^{-1}. The influence of NH_3 is more controversial. The study of Machalek et al. (2003) found that NH_3 inhibits the oxidation of Hg^0 inside SCR. Niksa and Fujiwara (2005) theoretically calculated this process and addressed the inhibition mechanism by NH_3 competing with atomic Cl on active sites. However, on-site measurements in three coal-fired power plants showed the opposite results, that is, the increase of NH_3 injection rate promotes Hg^0 oxidation (L. Zhang et al., 2013b). Possible chemical mechanism was proposed for the observed oxidation, but requires further investigation. The concentrations of NO, SO_2 and total mercury and the type and on-duty time of the SCR catalyst also affect the heterogeneous oxidation processes inside SCR (Winberg et al., 2004; Niksa and Fujiwara, 2005; L. Zhang et al., 2013b). Field tests in coal-fired power plants showed an average Hg^0 oxidation rate of 71% with a range of 34–85% (Chen et al., 2008; Zhang, 2012; L. Zhang et al., 2013b).

2.2.2 Mercury transformation in electrostatic precipitator (ESP)

Due to its high PM removal efficiency and relatively low cost, ESP is the most widely used PM controller in coal-fired power plants. Over 99% of Hg_p is removed inside ESP (Wang et al., 2010a). A small portion of Hg^{2+} can also be adsorbed onto fly ash and removed by ESP. The Hg^{2+} capture rate is determined by the unburned carbon (UBC) on fly ash (Senior and Johnson, 2005). The total mercury removal efficiency of ESP is usually in the range of 20–40% at ~5% UBC content of fly ash. Besides the UBC, the surface property, size, porous structure and mineral composition of fly ash affect the mercury capture rate of ESP as well (Lu et al., 2007). When coal with high chlorine content is burned, more UBC is generated on fly ash and more Hg^{2+} and Hg_p are formed in flue gas, which in turn increase the mercury capture rate inside ESP. Improvement of ESP for capturing fine particles (e.g., adding electric fields inside ESP) will also increase mercury removal efficiency. Inter-conversion between Hg^0 and Hg^{2+} occurs inside ESP (Zhang, 2012). The charging anode of ESP can neutralize Hg^{2+} and convert it to Hg^0, while Hg^0 in flue gas continues to be oxidized to Hg^{2+} via heterogeneous reactions in ESP under temperatures of 150–200°C. Therefore, Hg^0 concentration can either increase or decrease inside ESP depending on the processes interplay. On-site measurements showed an average mercury removal efficiency of 29% for ESP with a large range of 1–74% (Goodarzi, 2004; Guo et al., 2004; Kellie et al., 2004; Tang, 2004; Duan et al., 2005; Lee et al., 2006; Chen et al., 2007; Yang et al., 2007; Wang et al., 2008; Zhou et al., 2008; Kim et al., 2010b; Shah et al., 2010; ICR, 2010; Wang et al., 2010a; Zhang et al., 2012a). Nevertheless, ESP installed after a CFB boiler can achieve an average of 74% mercury removal due to the high Hg_p proportion in flue gas (Chen et al., 2007; ICR, 2010; Zhang, 2012).

2.2.3 Mercury transformation in fabric filter (FF)

A higher PM removal efficiency can be achieved by FF than by ESP, especially for fine particles. FF is increasingly applied in coal-fired power plants and industrial boilers in the need of fine particle ($PM_{2.5}$ or PM_1) control. FF has mercury removal efficiencies of 9–92% with an average of 67% (Chen et al., 2007; Shah et al., 2008; Wang et al., 2009; ICR, 2010). Besides Hg_p, FF can also remove over 50% of Hg^{2+}. During the filtration, contact between flue gas and the particles on the cake layer promotes adsorption of Hg^{2+} onto fly ash (Zhang, 2012). The properties of fly ash have the most significant impact on Hg^{2+} adsorption. The dust cake layer can also facilitates the oxidation of Hg^0 (Wang et al., 2016a).

Some plants apply ESP-FF hybrid precipitator to improve the fine particle removal efficiency. Limited studies suggested an overall mercury removal rate of 39% in ESP-FF hybrid precipitator (S. X. Wang et al., 2014).

2.2.4 Mercury transformation during wet flue gas desulfurization (WFGD)

WFGD is the most widely used APCD for SO_2 control in coal-fired power plants. During sulfur (mainly SO_2) scrubbing process, Hg^{2+} is also removed in WFGD. The average mercury removal efficiency of WFGD is 64%, ranging from 56% to 88% (Lee et al., 2006; Chen et al., 2007; Kim et al., 2010b; Wang et al., 2010a). Insoluble Hg^0 passes through WFGD without being captured. Chemical reduction of the dissolved Hg^{2+} reduces total mercury removal efficiency in WFGD due to re-volatilization of Hg^0 (Wo et al., 2009; Ochoa-González et al., 2013). Flue gas and slurry composition, operating temperature, limestone injection rate, and slurry pH are the key factors affecting the re-volatilization of Hg^0 (Acuña-Caro et al., 2009; Ochoa-González et al., 2012; Schuetze et al., 2012). WFGD is the crucial step in the co-benefit mercury control technologies in coal-fired power plants. The applications of high-chlorine coal, SCR and halogen addition can increase the Hg^{2+} proportion in flue gas before WFGD, which will enhance the overall mercury capture efficiency of WFGD. Therefore, the optimized strategy for WFGD is to stabilize the Hg^{2+} in the WFGD slurry to prevent mercury re-volatilization. The overall mercury removal efficiency of WFGD is on average 45% with a range of 10–85% (Yokoyama et al., 2000; Kilgroe et al., 2002; Ito et al., 2006; Lee et al., 2006; Meij and Winkel, 2006; Chen et al., 2007; Kim et al., 2010b; Wang et al., 2010a).

2.2.5 Mercury transformation in wet scrubber (WS)

Coal-fired industrial boilers are usually in a smaller scale compared with the utility boilers. The PM control for industrial boilers are not as advanced as those for power plants in developing countries. For example, WS is most widely adopted in China's industrial boilers. The proportion of Hg_p in flue gas of industrial boilers (1–3%) is not as high as that of power plants because of the shorter formation times of Hg_p in industrial boilers, especially in small-scale ones. Consequently, the Hg_p removal rate of WS is only about 50% (Zhang, 2012). SO_2 in flue gas can dissolve in water and form SO_3^{2-}, which could be a reducing agent for Hg^{2+}, leading to low Hg^{2+} capture rates in WS (Chang and Ghorishi, 2003; Omine et al., 2012). The overall mercury removal rate of WS is 23% on average with a range of 7–59% (Zhang, 2012).

2.3 Mercury speciation profile for coal-fired boilers

Mercury speciation profiles in the flue gas from coal combustion are summarized in Table 1, which considers the transformation of mercury species across different types of APCDs (Goodarzi, 2004; Guo et al., 2004; Kellie et al., 2004; Tang, 2004; Duan et al., 2005; Lee et al., 2006; Zhou et al., 2006; Chen et al., 2007; Yang et al., 2007; Chen et al., 2008; Shah et al., 2008; Wang et al., 2008; Zhou et al., 2008; Kim et al., 2010b; Shah et al., 2010; Wang et al., 2010a; Zhang, 2012; Zhang et al., 2012a; L. Zhang et al., 2013b). When no APCD is applied, mercury speciation profile has the largest variability due to the different properties of coal burned. The average proportions of Hg_p are all below 2% when PM control devices are installed. As commonly used for stoker-fired (SF) industrial boilers, WS removes a large proportion of Hg_p and a small proportion of Hg^{2+}, resulting in a decrease of Hg_p percentage and a slight increase of Hg^0 percentage compared with the case of non-control. The average percentages of Hg^0 and Hg^{2+} in the flue gas exhausted from ESP are 58% and 41%, respectively. The presence of CFB boiler can increase the proportion of Hg^0. The proportions of Hg^0 and Hg^{2+} are similar in the flue gas after FF, although with large variability. For the combination of ESP+WFGD, the proportion of Hg^0 reaches as high as 84%. With the existence of SCR, the average proportion of Hg^0 is not as high as that for the combination of ESP+WFGD because of the high oxidation rate of Hg^0 inside SCR. Large uncertainties still exist in flue gas from the combinations of PC+FF, PC+FF+WFGD and CFB+ESP, since scarce speciation data is available.

3 Mercury speciation and transformation in flue gases from non-ferrous metal smelters

3.1 Mercury speciation in the roasting/smelting furnaces

Non-ferrous metals (zinc, lead, copper and industrial gold) are mainly produced from sulfide ores. Usually, mercury is released from concentrates to flue gases during the pyrometallurgical processes of non-ferrous metals. A typical pyrometallurgical process requires four stages, including dehydration, smelting/roasting, extraction, and refining (Wang et al., 2010b; Zhang et al., 2012b; Wu et al., 2015). Approximately 1% of mercury in concentrates is released to flue gas in the dehydration kiln, where the temperature varies from 150–700°C (Song, 2010). Mercury in concentrates is mainly released during smelting/roasting stage. The temperatures in the smelting/roasting, thermal extraction and thermal refining stages are all higher than 800°C (Li et al., 2010; Wang et al., 2010b). The Hg-S and Hg-O bonds are broken under such high temperatures (Hylander and Herbert, 2008). Almost all mercury compounds are thermally dissociated into Hg^0 considering the thermodynamic stability of Hg^0 at this temperature (Wang, 2011). Mercury release rates during these stages are generally over 98% (Song, 2010; Li et al., 2010; Wu et al., 2015). The case in the industrial gold smelting process is an exception. Based on our on-site measurements, only 85% of the mercury in gold concentrate evaporates into the flue gas with the roasting temperature at 600°C (Yang, 2015). The low mercury release rate in the tested gold smelter may be related to chemical properties of mercury and gold. According to a previous study (Li, 1990), mercury at certain chemical speciation in gold ores only releases when the temperature exceeds 780°C. The released Hg^0 would be transformed to Hg^{2+} or Hg_p by catalytic oxidation in the flue gas with the existence of gas phase oxidants such as atomic Cl (Galbreath and Zygarlicke, 2000; L. Zhang et al., 2013a).

3.2 Mercury transformation across APCDs for the roasting/smelting flue gas

Flue gases from the four stages typically go through dust collectors to remove particles. FF or ESP is generally adopted for flue gases from the dehydration, extraction and refining stages, whereas a combination of waste heat boiler, cyclone and ESP is used for the roasting/smelting flue gas (Wu et al., 2012; UNECE, 2013). The flue gas is then cleaned in a purification system including flue gas scrubber (FGS) and electrostatic demister (ESD) before entering the acid plant for SO_2 recovery (see Fig. 2). To minimize heavy metal emissions, the roasting/smelting flue gas could also require additional mercury removal after the purification system (UNECE, 2013). Since the roasting/smelting stage releases the most mercury, previous studies focus on mercury transformation and removal inside APCDs for the roasting/smelting flue gas (Zhang et al., 2012b; Wu et al., 2015). Figure 3 shows the mercury speciation after APCDs for non-ferrous metal smelters. Overall, the Hg_p proportion is less than 5% for all non-ferrous metal smelters. Hg^0 is the dominant species in the flue gas after the purification devices in most situation since most Hg^{2+} has been removed. However, when the flue gas goes through the acid plant, the share of Hg^{2+} increases to 80-98%.

3.2.1 Mercury transformation in the dust collectors

Dust collectors can remove >99% of particles and therefore Hg_p is mostly removed simultaneously. Hg_p proportion after dust collectors is less than 5% (Zhang et al., 2012b; Wu et al., 2015). Hg^0 can be homogeneously or heterogeneously oxidized in the flue gas, while the charging anode in the ESP can reduce Hg^{2+} to Hg^0. Therefore, the resulting mercury speciation profile after the dust collectors depends on the competition between Hg^{2+} reduction and Hg^0 oxidation. The proportion of Hg^{2+} after dust collectors varies a lot (4–85%) among different tested smelters (Zhang et al., 2012b; Wu et al., 2015). The total mercury removal efficiency of dust collectors is usually less than 20%. Test results of three zinc smelters showed mercury removal efficiencies of 9–12% (Wu et al., 2015). The study of Li et al. (2010) shows lower mercury removal efficiencies of dust collectors (1–5%). ESP plays the most important role in mercury removal for roasting/smelting flue gas. Zhang et al. (2012b) found an average mercury removal rate of 12%, which is much lower than the efficiency of ESPs in coal-fired power plants, because of two reasons. Firstly, higher temperature of ESPs in smelters (300–350°C compared to more or less 150°C in coal-fired power plants) would restrain the Hg^0 condensation and Hg^{2+} absorption processes (Meij and Winkel, 2006). Secondly, although the dust concentrations in the flue gases of the coal-fired power plants and the non-ferrous metal smelters are at the same level, mercury concentration in flue gas of non-ferrous metal smelters is two to three orders higher than that in the flue gas of coal-fired power plants (Tang et al., 2007; Wang et al., 2010a,b; Zhang, 2012; Zhang et al., 2012a,b; Wu et al., 2015). Under such conditions, there might not be sufficient active sites on the particles for mercury adsorption in the flue gas of non-ferrous metal smelters.

3.2.2 Mercury transformation in purification systems

The purification system generally includes FGS and ESD. Unlike WS or WFGD for SO_2 control in coal combustion, FGS in non-ferrous metal smelters uses diluted sulfuric acid to capture SO_2 and SO_3. The yield from FGS is waste acid, which will be treated to acid sludge. ESD is employed to remove water vapor from flue gas. Li et al. (2010) and Wang et al. (2010b) found that mercury removal efficiency in FGS was 11–22%, whereas ESD removed 10–42% of total mercury in the flue gas. The overall mercury removal efficiency of the purification systems in six tested plants by Zhang et al. (2012b) varies in the range of 72–99%. Studies of Zhang et al. (2012b) and Kim et al. (2011) show that higher Hg^{2+} in the flue gas entering the purification system leads to higher mercury removal efficiency considering the high solubility of Hg^{2+} in water and sulfuric acid. In addition, Hg^0 would condense to liquid metallic mercury when the temperature of flue gas decreases from 300°C to approximately 25°C at the outlet of the purification system (Song, 2010). Previous studies have observed liquid Hg^0 in the removed waste acid (Wang, 2011). The dominant mercury species after the purification system is generally Hg^0, with a proportion 43–96% (Wang et al., 2010b; Zhang et al., 2012b; Wu et al., 2015).

3.2.3 Mercury transformation in other mercury removal systems

Mercury in the flue gas can be removed by other techniques including Boliden-Norzink process, Bolchem process, Outokumpu process, sodium thiocyanate process, selenium scrubber, activated carbon filters, and selenium filter (UNECE, 2013). The removal mechanisms in these processes are either to oxidize Hg^0 into Hg^{2+}or Hg^+ with strong oxidants and then remove oxidized mercury, or to capture Hg^0 with specific adsorbents. The Boliden-Norzink process, the most widely used process in non-ferrous metal smelters, has been installed in more than 40 smelters globally. On-site measurements indicated that its mercury removal efficiency is 83–92% (Wang et al., 2010b; Li et al., 2010; Wu et al., 2015). In the Boliden-Norzink process, Hg^0 in the flue gas is oxidized to Hg_2Cl_2 by solution containing $HgCl_2$. The yield Hg_2Cl_2 is removed from the circulating solution and then either used for mercury production or stored, whereas the solution is reused after regeneration. Other processes are not as commercialized as the Boliden-Norzink process.

3.2.4 Mercury transformation in the acid plants

An acid plant generally includes dehydration tower, conversion tower and absorption tower. Dehydration tower uses 93–95% sulfuric acid to remove the water vapor. Conversion tower converts SO_2 into SO_3 with vanadium catalysts. Absorption tower absorbs SO_2 with 98% sulfuric acid. Tests in one zinc smelter with a mercury reclaiming tower indicates that mercury speciation profile (Hg^0:Hg^{2+}:Hg_p) after the acid plant is 6:90:4 (Wang et al., 2010b). Wu et al. (2015) found that the proportion of Hg^{2+} increased from 4% to 98% when passing the acid plant. The total mercury removal efficiency in the acid plant can reach 83%. On-site measurements in six smelters by Zhang et al. (2012b) showed that the dominant species was Hg^{2+} after the acid plant with the double-conversion-double-absorption process, while Hg^0 became the dominant species after the single-conversion-single-absorption process. The net reaction of mercury in the acid plant is the oxidation of Hg^0, either by the oxidants in flue gas under the vanadium catalysts in the conversion tower or by the concentrated sulfuric acid. However, further studies are required to understand the oxidation mechanisms.

3.3 Mercury speciation profile for non-ferrous metal smelters

Mercury speciation profiles in the flue gases from non-ferrous metal smelters are summarized in Table 2. In early mercury emission inventories, the relative emission proportions (REPs) among Hg^0:Hg^{2+}:Hg_p species for non-ferrous metal smelters were estimated to be 80:15:5 (Pacyna and Pacyna, 2002; Streets et al., 2005; Pacyna et al., 2006; Wu et al., 2006). However, recent field tests found that the proportion of Hg^{2+} could reach >90% for the smelting/roasting stage with acid plants (Wang et al., 2010b; Zhang et al., 2012b). Besides the smelting/roasting stage, mercury emissions from the slag dehydration and volatilization stages are also significant. According to field experiments in a zinc smelter (Wang et al., 2010b), the mercury emissions from these two stages were 95 g/d and 50 g/d, respectively, even higher than that from the roasting process (22 g/d). Therefore, the overall mercury speciation profile for non-ferrous metal smelters is not only affected by the roasting/smelting flue gases but also by the dehydration flue gas and the volatilization flue gas. Mass flow analysis in three zinc smelters indicates that mercury emissions from the slag dehydration stage, the slag smelting stage and the volatilization stage accounted for 54–98% of total emissions, with Hg^0 as the dominant form (Wu et al., 2015). When considering atmospheric mercury emissions from all thermal processes in addition to the roasting process, the emission proportion of Hg^{2+} is reduced to 29–51% (Wu et al., 2015). In lead smelters, the proportion of Hg^{2+} is about 40% when considering atmospheric mercury emissions from the extracting and reclaiming processes (Zhang et al., 2012b). The proportion of Hg^{2+} in all exhausted gases is 32–68% in copper smelters with the double-conversion-double-absorption process installed for the roasting flue gas (Zhang et al., 2012b). The mercury speciation profile (Hg^0:Hg^{2+}:Hg_P) in the exhausted flue gases in gold smelters with the double-conversion-double-absorption process is estimated to be 32:57:11 (Yang, 2015).

4 Mercury speciation and transformation in flue gas from cement clinker production

4.1 Cement clinker production processes

A mix of raw materials, mainly limestone, are heated up to over 1400°C and different compositions react to produce clinker. Additives, usually gypsum, are then mixed with clinker and milled to produce cement. The temperature of the final cement production is usually under 100°C. Results from temperature programmed decomposition (TPD) experiments indicate that mercury is not released from gypsum at such temperatures

(Rallo et al., 2010; López-Antón et al., 2011; Liu et al., 2013). Therefore, we only consider the clinker production process that includes shaft kilns, wet rotary kilns, dry rotary kilns and precalciner processes.

Precalciner process is usually composed of the raw mill system, the coal mill system, the kiln system and the kiln head system. Raw materials are ground and homogenized in the raw mill system. The fuel, usually coal, is prepared in the coal mill system including coal mill and FF. The kiln system for the production of cement clinker includes the preheater, the precalciner and the rotary kiln. The prepared raw materials, namely raw meal, enter the kiln system from one end of rotary kiln (kiln tail), and the coal powder is brought into the kiln system by air from the other kiln end (kiln head). The solid materials flow in opposite direction with the flue gas. The flue gas from kiln tail is used to preheat raw materials in raw mill and coal in coal mill. The flue gas from kiln head is de-dusted and then emitted into the atmosphere. All the dust collected by dust collector is recycled to kiln system.

4.2 Mercury behavior in cement clinker production process

The mercury behavior in cement production process is summarized as three stages: vaporization, adsorption and recycling (Sikkema et al., 2011) (see Fig. 4). At the vaporization stage, mercury in raw materials and fuel is vaporized into flue gas in the kiln system. Then part of the mercury in flue gas is captured by raw materials in the raw mill and coal in the coal mill when the flue gas is used to preheat solid materials, and part of the mercury in flue gas is also collected in the dust collector with dust. This process is called the adsorption stage. Finally, the mercury is cycled back into the kiln system with raw materials, coal and collected dust, which is the recycling stage. Therefore, there are three mercury cycles in the precalciner clinker production process. Mercury cycling in cement plants has been confirmed in field tests (Mlakar et al., 2010; Paone, 2010; Sikkema et al., 2011; Zheng et al., 2012). A transient model was developed to simulate mercury concentration in flue gas from kiln tail (Senior et al., 2010). This model was based on a series of mass balances from preheater to the whole process.

The three mercury cycles cause mercury enrichment in the clinker production process. F. Y. Wang et al. (2014) assessed mercury enrichment process using the ratio of mercury concentration in the exhausted flue gas to the equivalent mercury concentration. The equivalent mercury concentration was defined by dividing the total mercury input from raw materials and coal with the total amount of flue gas emerged in the kiln system. It was found that the mercury concentration was enriched by as high as 4–15 times in two Chinese cement plants. Another study also confirmed this point, with the mercury concentration enriched by over 10 times (Mlakar et al., 2010).

Mercury enrichment can affect its emission from cement plants. The cement clinker production process has two modes depending on the operation of raw mill. When the raw mill is on (operation mode), the flue gas flows through raw mill first and then emitted into the atmosphere after dust removal. When the raw mill is off (direct mode), the flue gas directly flows through the FF after the raw mill and emits into the atmosphere. In operation mode, a larger proportion of mercury in flue gas is recirculated and enriched in the system because the combination of raw mill and FF has a higher mercury removal efficiency than FF alone. Therefore, switching between the two modes significantly changes mercury enrichment and concentration in flue gas. It should be noted that mercury concentration in the clinker is low. If no filtered dust is discarded, over 90% of mercury input from raw materials and coal is eventually emitted into the atmosphere (Paone, 2008; Linero, 2011; Hoenig and Zunzer, 2013).

4.3 Mercury transformation during cement clinker production process

In mercury vaporization stage, mercury in raw materials and coal is released into the flue gas. Field tests in power plants of previous studies indicated that almost all of the mercury in coal (>99%) was vaporized into the flue gas as the elementary form because of the high temperature in coal-fired boilers, which is usually higher than 1000°C (Tang et al., 2007; Wang et al., 2010a; Zhang et al., 2012a). For the cement clinker production process, mercury in raw materials and coal is mostly released to the flue gas. Mercury concentration in clinker was less than 5 ng/g, accounting for only 1.9–6.1% of the total mercury (F. Y. Wang et al., 2014). The compounds of mercury silicates might be the main chemical forms of mercury in clinker (Schreiber et al., 2005). Temperature of raw materials increases continuously from 400°C at the inlet of the preheater to over 1400°C in the rotary kiln. Different mercury species have different decomposition and boiling temperatures, as summarized in one previous study (Zheng et al., 2012). Further studies on identification of mercury species in raw meals are needed to understand the mechanism of mercury vaporization in kiln system.

Mercury is oxidized homogeneously and heterogeneously in flue gas. As analyzed by F. Y. Wang et al. (2014), a series of operational conditions in the cement clinker production process can promote mercury oxidation. The oxidation of mercury is usually kinetically limited (Senior et al., 2000; Niksa et al., 2001; Wilcox et al., 2003; Krishnakumar and Helble, 2007; Liu et al., 2010). Residence time over 20 s provides enough reaction time for mercury oxidation. The high concentration of PM in flue gas, usually over 10 g/m^3, can catalyze the oxidation; and the addition of Fe-containing material in raw materials can provide more active sites for heterogeneous mercury oxidation (Dunham et al., 2003; Galbreath et al., 2005; Bhardwaj et al., 2009). Vaporized Hg^0 in the kiln system is oxidized during the cooling process of flue gas. Considering that Hg^{2+} can be easily adsorbed onto the surface of PM in flue gas and the PM concentration in flue gas is high, the proportion of Hg_p is therefore high. Mercury speciation in the flue gas entering the raw mill system was measured in three cement plants (F. Y. Wang et al., 2014). The proportion of Hg^{2+} was in the range of 64–76%, while the proportion of Hg_p was 21–27%. Mlakar et al. (2010) found that the proportion of Hg_p in another plant was even higher, ranging in 15–77%. The high proportion of Hg^{2+} and Hg_p can cause a high mercury removal efficiency in APCDs and other facilities, including dust collectors, raw mill and coal mill. Mercury removal efficiencies of raw mill with FF and coal mill with FF could reach 86–89% and 94–95%, respectively (F. Y. Wang et al., 2014). The mechanisms of mercury removal in raw mill and FF are different. The removal of Hg_p in FF and adsorption of Hg^{2+} onto the filter cake are considered to be the predominant mechanism in FF (Chen et al., 2007; Wang et al., 2010a). At mercury recycling stage, the removed mercury in raw mill, coal mill and dust collectors is eventually cycled into kiln system with raw mill, coal powder and dust, respectively. Overall, because of the existing mercury cycling and a series of operational conditions promoting mercury oxidation, mercury speciation during clinker production is dominated by Hg^{2+} and Hg_p.

4.4 Mercury speciation profile for cement plants

The mercury emissions from the cement clinker production process were previously considered to be composed of 80% Hg^0, 15% Hg^{2+} and 5% Hg_p (Streets et al., 2005). Recent field results (Mlakar et al., 2010; Won and Lee, 2012; F. Y. Wang et al., 2014) on mercury emission speciation of cement production are shown in Table 3. The proportions of different mercury species fluctuate at a wide range. Won and Lee (2012) found that Hg^{2+} only accounted for 15% of the total mercury emissions, while other studies (VDZ, 2002; Mlakar et al., 2010; Linero, 2011; F. Y. Wang et al., 2014) showed that Hg^{2+} was the dominant species accounting for 60% to >90% of the total mercury. As discussed above, the mercury speciation and emission are largely variable because of the complicated mercury cycling and operational modes of the cement clinker production process. Previous estimates of mercury emission and speciation from cement clinker production have large uncertainties. More studies including field tests should be conducted to further understand the mechanism of mercury speciation and transformation in cement production.

5 Mercury speciation and transformation in flue gases from other emission sources

In this section, the behavior of mercury in flue gases from other emission sources, including iron and steel production, waste incineration, biomass burning, cremation, and PVC production, are introduced. Although there are still other mercury emission sources not discussed in this study, such as oil combustion, few field measurements are available for mercury speciation and transformation inside these sources.

5.1 Mercury speciation and transformation in flue gas from iron and steel production

Iron and steel production is composed of raw material preparation (rotary kilns for limestone and dolomite production and the coking process), sintering machine, blast furnace and convertor. In raw material preparation, limestone and dolomite are roasted in rotary kilns and coking coal is produced in coke oven. Iron ores, coke and limestone (dolomite) are then mixed and roasted in the sintering machine, namely the sintering process. Products of these two stages are fed to the blast furnace where sinter, coke and limestone are smelted to produce iron, and then the iron is smelted in a convertor to produce steel. There is also another process using steel scrap to produce steel, called electric furnace. To increase the utilization efficiency of energy, coal gas emerged in the coke oven, blast furnace and convertor is collected and burned to generate electricity. The operational conditions in different stages are quite different. The mercury behavior in iron and steel plants is therefore quite complicated.

Mercury is vaporized in high-temperature facilities, including coke oven, sintering machine, blast furnace and convertor. Mercury in the flue gas is oxidized homogeneously and heterogeneously. Part of the mercury is removed in dust collectors and flue gas desulfurization devices, and the remaining mercury in flue gas is emitted into the atmosphere. Field tests indicated that the mercury release rates in coke oven and sintering machine were lower than that in coal-fired boilers (>99%) because of the lower temperature in these facilities (Wang et al., 2016b). Previous studies indicated that the mercury emissions from sintering machine accounted for about 90% of total emissions from iron and steel plants (Fukuda et al., 2011). A speciation profile of 80% Hg^0, 15% Hg^{2+} and 5% Hg_P was applied in Streets et al. (2005). However, oxidized mercury was found to be the predominant species in our recent study (Wang et al., 2016b). The proportion of Hg^{2+} in flue gas reached as high as 59–73% and the proportion of Hg_P was under the detection limit because of the installation of ESPs for the examined iron and steel plants (Wang et al., 2016b). The high PM concentration in flue gas and Fe on PM could promote mercury oxidation in flue gas. More field tests need to be conducted on mercury speciation profile of this industry in the future.

5.2 Mercury speciation and transformation in flue gas from waste incineration

Waste incineration is a potential predominant source in the global mercury emission inventory. The major incineration types are municipal solid waste (MSW) incineration, medical waste incineration and industrial/hazardous waste incineration. A significant proportion of mercury (80–96%) in the MSW releases from the incinerator into the flue gas is in the form of Hg^0 at 850–1000°C (Park et al., 2008). Grate furnace combustor (GFC) and circulation fluidized bed combustor (CFBC) are the two most commonly used incinerators. The flue gas from CFBC has a larger proportion of Hg_p than that from GFC. Typical APCDs for incinerators are combinations of semi-dry or dry flue gas deacidification (SD-FGD or D-FGD) for SO_2 and HCl removal and dust controller (e.g., WS+ESP, FF, FF+WS, etc.). SCR is sometimes used as well for NO_x control. Activated carbon injection (ACI) is used for the control of persistent organic pollutants (POPs), which is required for incinerators in China.

The overall mercury removal efficiency of the APCDs for MSW incineration ranges from 60% to over 99% (Zhang et al., 2008; Takahashi et al., 2012). Previous studies in Europe and the USA indicated that the Hg^{2+} proportion in the exhausted flue gas ranges from 75% to 85%(Pacyna and Münch, 1991; Carpi, 1997). A Korean study found the Hg^{2+} proportion in MSW incinerators to be in the range of 78–89%, and that in industrial waste incinerators are even as high as 96.3–98.7% (Park et al., 2008). Kim et al. (2010a) tested two medical waste incinerators with SD-FGD+FF+WS and got the Hg^0 proportion to be 43.9% and 96.8% respectively. A Japanese study showed that an industrial waste incinerator with WS and wet ESP has the Hg^0 proportion of 92.7% (Takahashi et al., 2012). Based on field measurements in eight MSW incinerators in China, Chen et al. (2013) found that average Hg^{2+} proportion in flue gas from the outlet of GFC+SD-FGD+ACI+FF is 96%, while that for CFBC+SD-FGD+ACI+FF is 64%. High chlorine content in the waste results in high Hg^{2+} proportion in the flue gas. Limestone slurry or powder sprayed in SD-FGD or D-FGD absorbs a large amount of Hg^{2+} and activated carbon adsorbs a large amount of both Hg^0 and Hg^{2+}. Particles from SD-FGD and ACI are captured by the downstream FF. Hg_p is removed by all types of dust controllers. The high Hg^{2+} formation rate due to the oxidative condition in flue gas and the high Hg^{2+} removal rate by APCDs (especially SD-FGD, FF and ACI) cause the significant variation in mercury speciation profiles for incinerators.

5.3 Mercury speciation and transformation in flue gas from biomass burning

Biomass burning mainly includes biomass fuel burning and open biomass burning. Biomass fuel can be divided into fuel woods, crop residues and biomass pellets. Usually, there is no APCD for biomass burning. Huang et al. (2011) tested four different types of wood fuels and found the Hg^0 proportion to be 95–99% and the rest is basically Hg^{2+}. Wei (2012) found that Hg^0 in flue gas from biomass burning is 70–90% of total mercury while that of Hg^{2+} ranges from 5% to 9%. Hg_p proportion differs a lot between different biomass fuel types: 12%, 25% and 1% for fuel wood, crop residues and biomass pellets, respectively. Hu et al. (2012) differentiated the emission factors for biomass burning and cooking/space heating in rural areas to be 0.035 and 0.515 g Hg/t biomass burned, respectively. W. Zhang et al. (2013) tested 25 types of fuel wood, 8 types of crop residues and 2 types of biomass pellets, and found that the mercury emission rate during biomass burning is 78–99% while the remainder stays in the residue. The mercury speciation profile (ratio of Hg^0, Hg^{2+} and Hg_p to total Hg) for fuel wood was 76%, 6% and 18%, and that for crop residue was similar (73%, 4% and 23%). However, the speciation profile for biomass pellets is quite different. Due to the more complete combustion, Hg^0 accounts for as high as 97% in the flue gas from of biomass pellets combustion. W. Zhang et al. (2013) calculated mercury emission from biomass burning in China and gave the shares of Hg^0, Hg^{2+} and Hg_p at 74%, 5% and 21%, respectively. Open biomass burning generally involves forest wildfires, grassland/savanna wildfires, and agriculture residue burning. Friedli et al. (2003) investigated the mercury speciation from burning of temperate North American forests through both laboratory and airborne measurements. Their research showed that the dominant species is Hg^0, accounting for 87–99% of the total mercury, and the rest is mainly Hg_p.

5.4 Mercury speciation and transformation in flue gas from cremation

Researches on mercury speciation and transformation in flue gas from cremation are very limited. Takaoka et al. (2010) conducted field measurements in seven crematories in Japan, two of them without any APCDs, one with ESP and four with FF for particle control. Advanced APCDs such as catalytic reactor and activated carbon filter are installed in three of the tested crematories. In the exhausted flue gases, Hg^0 is averagely the dominant mercury species but with significant variation (25–99%). Extremely large uncertainties exist in this sector due to the large diversity of mercury content in human body and whether the dental amalgam is applied.

5.5 Mercury speciation and transformation in flue gas from PVC production

Aside from combustion and some high-temperature industrial processes, there are some other processes with intentional mercury use that also have mercury emissions. The production of polyvinyl chloride (PVC) with the calcium carbide process utilizes a catalyst containing large amounts of mercury. Ren et al. (2014) conducted on-site measurements in a PVC production line and found that 71.5% of the total mercury was lost from the catalyst, most of which was recovered by the mercury remover, accounting for 46% of the total mercury. The total mercury emitted to the atmosphere only accounted for less than 1% of the total mercury in the catalyst. The speciation tests indicated that most of the mercury escaped from the catalyst was Hg^0, as no Hg^{2+} was detected virtually.

6 Comparison of mercury speciation profiles in different countries and regions

Table 4 summarizes the sectoral mercury speciation profiles in different countries and regions (Pacyna et al., 2006; AMAP/UNEP, 2008; Chrystall and Rumsby, 2009; Kim et al., 2010a; Lin et al., 2012; Nelson et al., 2012; Zhang et al., 2015). China and South Korea have compiled extensive speciation profiles based on observational data collected at anthropogenic mercury emission sources. The inventories for Europe and New Zealand used same speciation data as the global inventory for coal combustion, which is close to the results of South Korea. China has different speciation data for coal combustion, where the proportion of Hg^0 is higher than that reported in other countries. This is probably because the high WFGD installation rate in China results in higher Hg^{2+} removal efficiency. Mercury speciation for coal-fired power plants, industrial and residential coal combustion are also different. Residential coal combustion has the lowest Hg^{2+} proportion while industrial coal combustion has the highest. This is mainly influenced by the boiler type and the APCDs applied. Residential stove has a short temperature-decrease time, which reduces formation of Hg^{2+}. The APCDs applied for industrial coal combustion have a lower Hg^{2+} removal efficiency than those applied for coal-fired power plants.

Global inventory applied similar speciation profiles for most other industrial sectors, i.e., 80% Hg^0, 15% Hg^{2+} and 5% Hg_P. The inventories estimated in China and South Korea provide speciation profiles for different sectors. The sectors of non-ferrous metal smelting (including zinc, lead and copper), cement production and iron and steel production in China have higher Hg^{2+} proportions than most of the other countries, which is caused by catalytic mercury oxidation in acid plants in non-ferrous metal smelters and the intensive heterogeneous mercury oxidation in cement plants and steel plants. The higher Hg^{2+} proportions imply that mercury emission from East Asia could have more local environmental impacts than previously expected. Our recent study (L. Wang et al., 2014) indicated that anthropogenic sources in China contribute 35–50% of the total mercury concentration and 50–70% of the total deposition in polluted regions in China.

7 Conclusions

The initial speciation of mercury after the boiler, smelter or kiln varies significantly because of the diverse qualities of coals or raw materials. Nearly all mercury in coal is released into the flue gas in the form of Hg^0 during combustion. Hg^0 is the predominant mercury species in exiting flue gases from coal-fired power plants mainly due to the high Hg_P removal efficiency of ESP or FF and the high Hg^{2+} removal efficiency of WS or WFGD. The enhancement of Hg^0 oxidation in SCR and by halogen injection is effective for mercury emission control in coal-fired power plants. outlet of On the contrary, Hg^{2+} tends to be the principal form in the flue gases emitted from non-ferrous metal smelters, cement plants and iron and steel plants. Catalytic metallic components and high PM concentrations in flue gases are the two primary causes. Flue gas purification systems and processes in acid plants for non-ferrous metal smelting contribute to the largest amount of mercury removal in non-ferrous metal smelters.

Specific mercury reclaiming tower in non-ferrous metal smelters preferentially releases Hg^0 to downstream flue gases. The key to mercury emission controls in cement plants is to break the mercury cycling processes during the dust recirculation for the kiln, raw mill and coal mill. Since Hg^{2+} dominates the mercury speciation of emissions from cement plants and iron and steel plants, WS or WFGD could be implemented for mercury abatement.

Mercury speciation profiles for key sources reported in recent studies are significantly different from those obtained in early studies. This is partially because the APCDs used in these sources have advanced in the past two decades. Another reason lies in the lack of on-site measurements in early emission estimates where certain speciation profiles were assumed. Adoption of different APCDs and use of different fuels or raw materials cause distinct differences found in mercury speciation profiles applied in different countries or regions. Large proportion of Hg^{2+} from non-ferrous metal smelters, cement plants and iron and steel plants calls for local attention. There are still large uncertainties in the speciation profiles at key sources, such as iron and steel plants, waste incineration and biomass burning. More on-site measurements for these sources should be carried out to complete the database of mercury emission speciation. Research is also needed in understanding the mechanism of mercury oxidation and adsorption in flue gases with different compositions, which benefits mercury emission controls. Accurate speciation profiles improve the performance of regional transport and dispersion models to better assess the environmental impacts of mercury emissions into the atmosphere.

Acknowledgment. This work was funded by Major State Basic Research Development Program of China (973 Program) (No. 2013CB430001 and No. 2013CB430003) and National Natural Science Foundation of China (No. 21307070).

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Table 1. Average speciation profiles (ranges) of mercury emissions from coal combustion by boiler type and control technology (%)

No.	Boiler type	APCD combination	Hg^0	Hg^{2+}	Hg_p	No. of tests
1	PC/SF	None	56 (8-94)	34 (5-82)	10 (1-28)	13
2	SF	WS	65 (39-87)	33 (10-60)	2.0 (0.2-4.5)	6
3	PC	ESP	58 (16-95)	41 (5-84)	1.3 (0.1-10)	31
4	PC	ESP+WFGD	84 (74-96)	16 (4-25)	0.6 (0.1-1.9)	7
5	PC	SCR+ESP+WFGD	74 (16-96)	26 (4-84)	0.2 (0.1-0.4)	6
6	PC	FF	50 (25-63)	49 (36-75)	0.5 (0.1-1.0)	3
7	PC	FF+WFGD	78	21	0.9	1
8	CFB	ESP	72	27	0.6	1

Notes: PC boiler – pulverized-coal boiler; SF boiler – stoker-fired boiler; CFB boiler – circulating fluidized bed boiler; WS – wet scrubber; ESP – electrostatic precipitator; FF – fabric filter; WFGD – wet flue gas desulfurization; SCR – selective catalytic reduction. References to Table 1 are listed in Section 2.3.

Table 2. Average speciation profiles of mercury emissions from non-ferrous metal smelters by control technology (%)

Metal type	APCD combinations	Hg^0	Hg^{2+}	Hg_p	Reference
Non-ferrous metal	N.S.	80	15	5	Streets et al. (2005) Pacyna et al. (2006) Wu et al. (2006)
Zinc	DC+ PS + MRT + AP_d	71	28	1	Wu et al. (2015)
Zinc	DC+ PS + AP_d	55	44	1	Zhang et al. (2012b) Wu et al. (2015)
Lead	DC+PS+ AP_s	40	60	0	Zhang et al. (2012b)
	DC+ PS + AP_d	39	61	0	Zhang et al. (2012b)
Copper	DC + PS + AP_d	50	50	0	Zhang et al. (2012b)
Gold	DC + PS + AP_d	32	57	11	Yang (2015)

Notes: N.S. – not specific; DC – dust collector; PS – purification system; MRT – mercury reclaiming tower; AP_d – acid plant with double-conversion-double-absorption processes; AP_s – acid plant with single-conversion-single-absorption processes.

Table 3. Average proportions of emitted mercury species from cement clinker production (%)

Production processes	Hg^0	Hg^{2+}	Hg_p	References
N.S.	80	15	5	Streets et al.(2005)
N.S.	85	15	0	Won and Lee(2012)
Precalciner process (raw mill off)	16.0	75.7	8.3	Mlakar et al. (2010)
Precalciner process (raw mill on)	43.1	45.5	11.4	Mlakar et al. (2010)
Precalciner process	9.2	90.8	0.0	F. Y. Wang et al. (2014)
Precalciner process	38.7	61.3	0.0	F. Y. Wang et al. (2014)
Precalciner process	23.4	75.1	1.6	F. Y. Wang et al. (2014)

Note: N.S. – not specific.

Table 4. Comparison of sectoral mercury speciation profiles for different countries and regions (%)

Countries or regions	**Global**			**China**			**South Korea**			**Europe**			**USA**			**Australia**			**New Zealand**		
Inventory year	**2005**			**2010**			**2007**			**2000**			**2005**			**2006**			**2008**		
Mercury emission source	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p
Coal-fired power plants	50	40	10	79	21	0	47	46	7	50	40	10	57	40	4	77	17	6	50	40	10
Industrial coal combustion	50	40	10	66	32	2				50	40	10							50	40	10
Residential coal combustion	50	40	10	82	17	1				50	40	10							50	40	10
Stationary oil combustion	50	50	0	50	40	10	23	10	68	50	50	0	61	28	12	77	17	6			
Mobile oil combustion	50	50	0	50	40	10	87	13	0	50	50	0	61	28	12	77	17	6			
Biomass fuel combustion	80	15	5	74	5	21															
Municipal solid waste incineration	20	60	20	96	0	4	36	61	3	25	58	17	61	28	12	77	17	6			
Cremation	80	15	5	96	0	4	65	12	23							80	10	10			
Zinc smelting	80	15	5	30	65	5	73	11	16	75	13	13	61	26	13	77	17	6	80	15	5
Lead smelting	80	15	5	57	38	5	38	8	54	75	13	13	61	26	13	77	17	6	80	15	5
Copper smelting	80	15	5	47	48	5	28	38	34	75	13	13	61	26	13	77	17	6	80	15	5
Large-scale gold production	80	15	5	80	15	5										77	17	6			
Artisanal and small-scale gold mining	100	0	0	80	15	5															
Mercury production	80	20	0	80	15	5															
Cement production	80	15	5	34	65	1	83	16	1	80	17	3				77	17	6	80	15	5
Iron and steel production	80	15	5	34	66	0	15	80	5	83	17	0	80	10	9	77	17	6	80	15	5
Chlor-alkali production	70	30	0	100	0	0				70	30	0				77	17	6			
References	AMAP/UNEP (2008) Pacyna et al. (2006)			Zhang et al. (2015)			Kim et al. (2010b)			Pacyna et al. (2006)			Lin et al. (2012)			Nelson et al. (2012)			Chrystall and Rumsby (2009)		

Figure Captions

Fig. 1. Mercury transformation and removal across APCDs in coal-fired power plants.

Fig. 2. Mercury transformation and removal in roasting/smelting flue gas.

Fig. 3. Mercury speciation after APCDs for non-ferrous metal smelters.

Fig. 4. Mercury transformation in the precalciner cement production process.

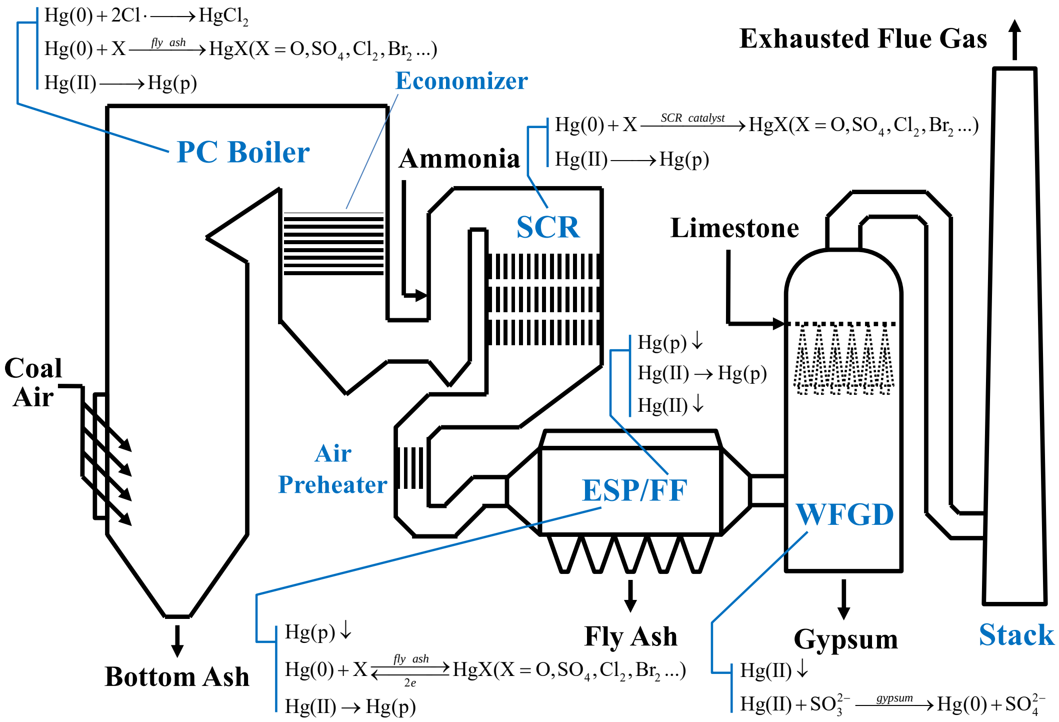


Fig. 1. Mercury transformation and removal across APCDs in coal-fired power plants.

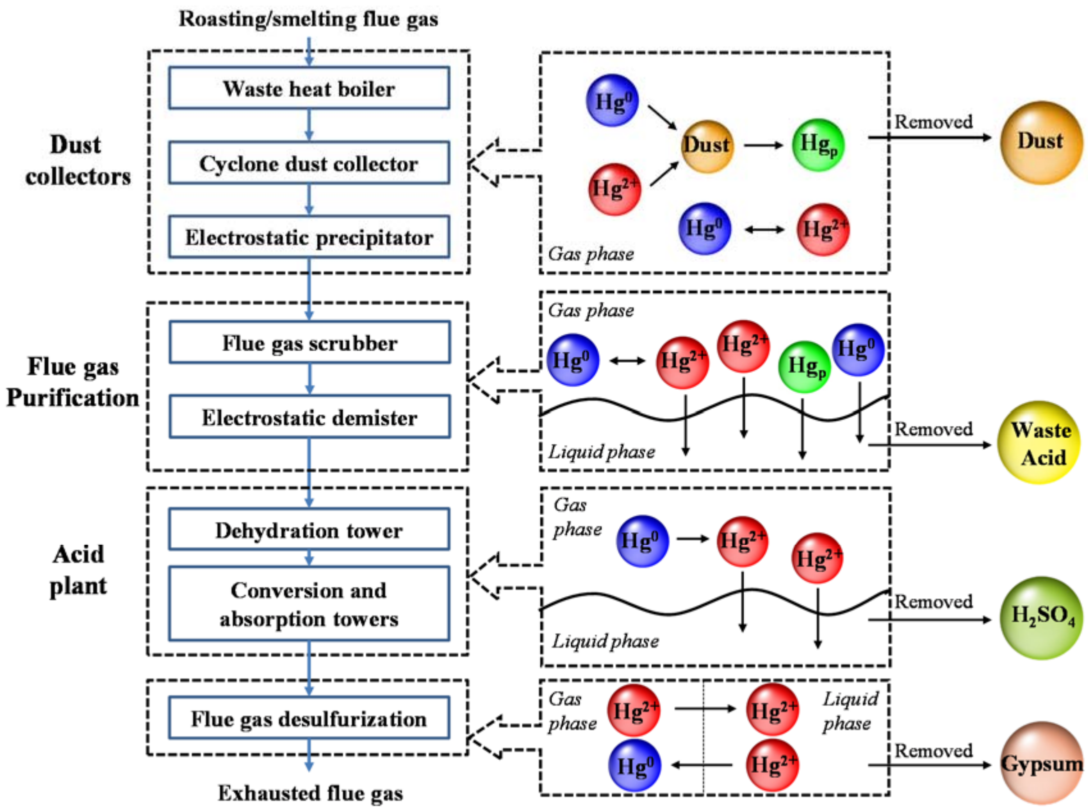
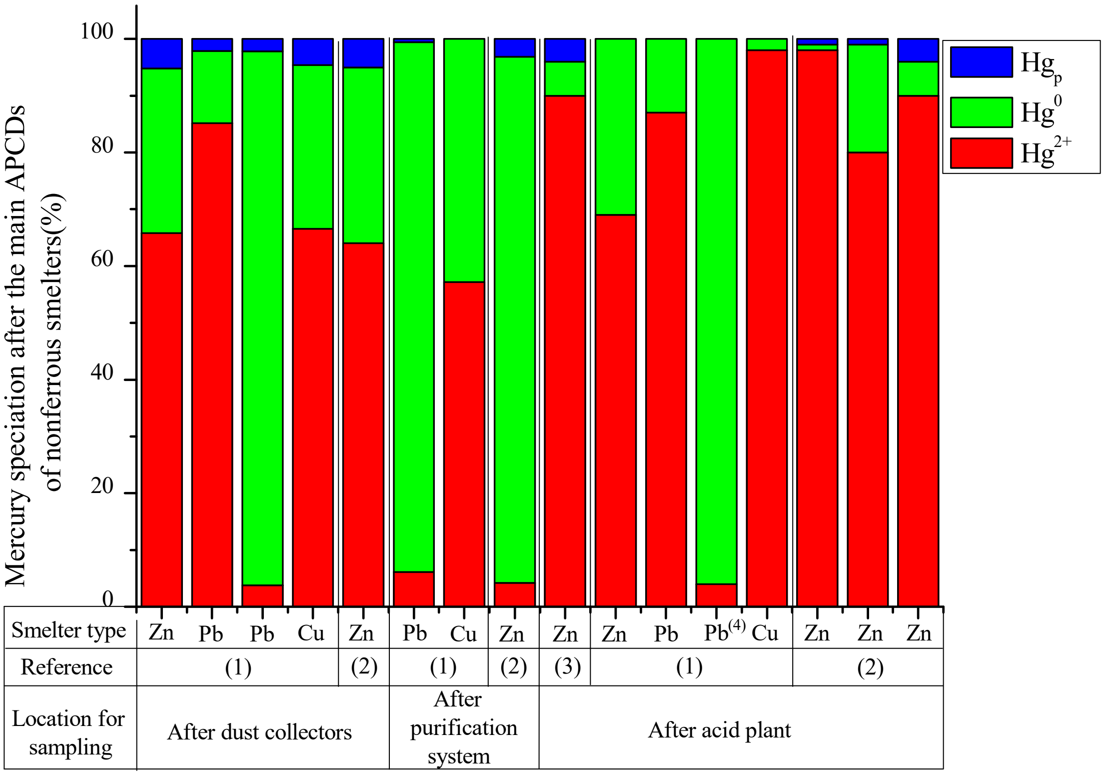


Fig. 2. Mercury transformation and removal in roasting/smelting flue gas.



Note: (1) Zhang et al., 2012; (2) Wu et al., 2015; (3)Wang et al., 2010;
(4) Acid plant with single contact and single absorption tower.

Fig. 3. Mercury speciation after APCDs for non-ferrous metal smelters.

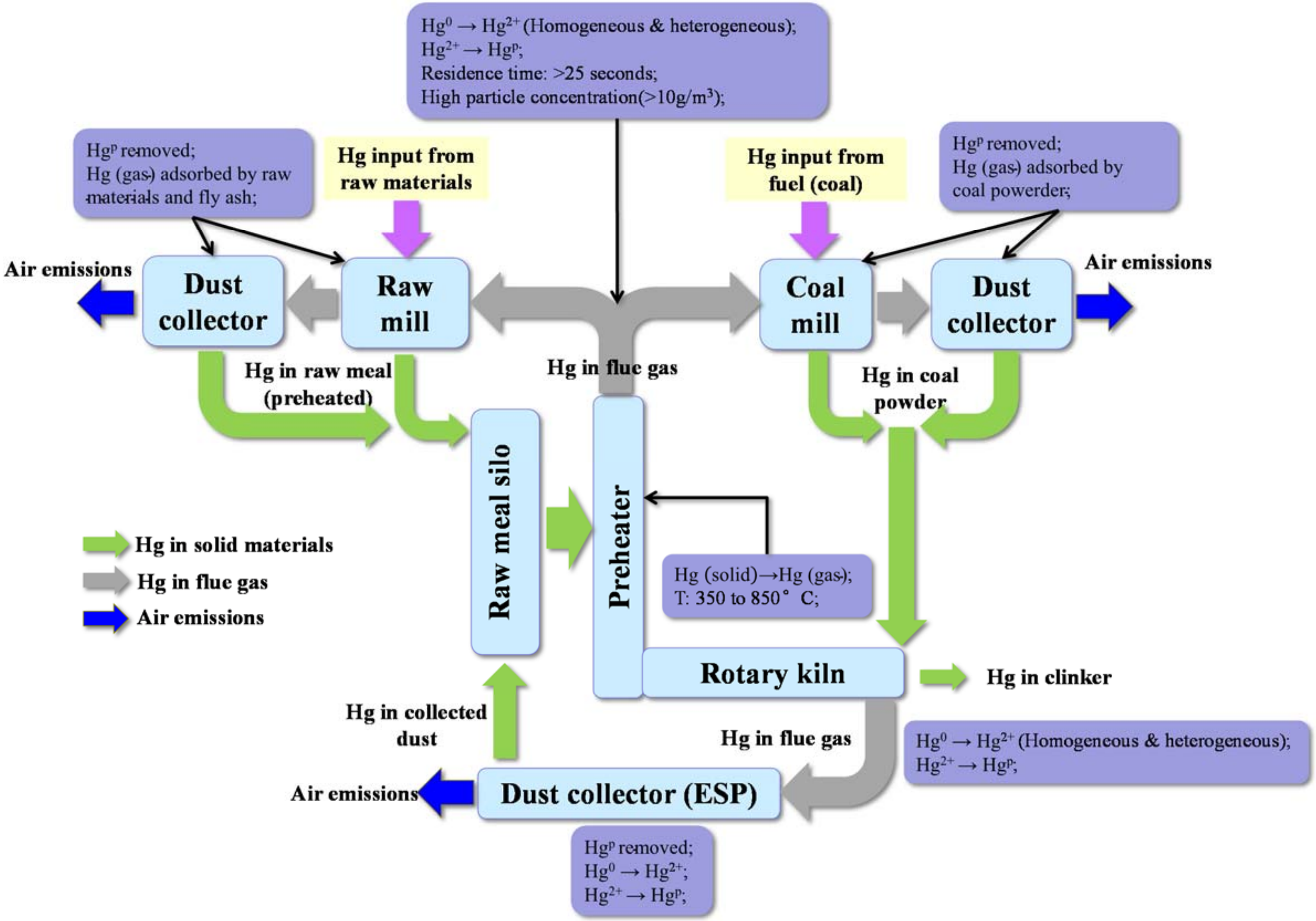


Fig. 4. Mercury transformation and flow in the precalciner cement production process.